

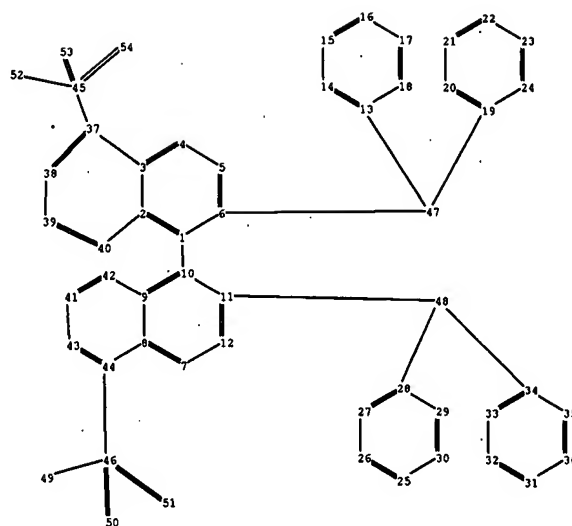
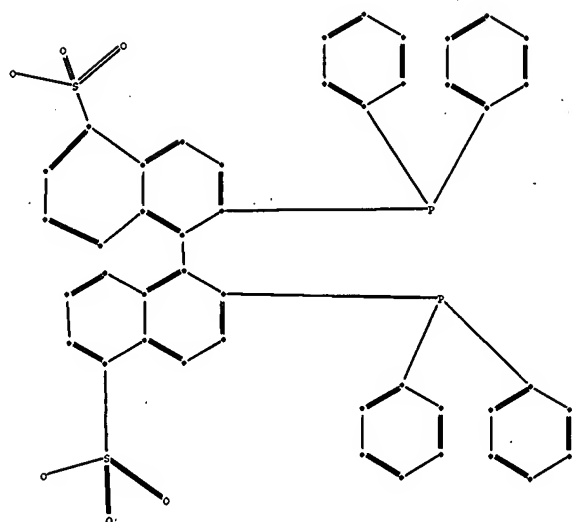
## EAST Search History

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	2	WO-9522405-\$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2007/08/03 18:52
S2	1603	(562/606,401).CCLS.	US-PGPUB; USPAT; USOCR	OR	OFF	2007/08/03 18:53
S3	2	EP-544455-\$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2007/08/06 10:07
S4	30	S2 and asymmetric adj hydrogenat\$	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2007/08/03 18:55
S5	6	("5563295").URPN.	USPAT	OR	ON	2007/08/03 19:01
S6	8	("5827794").URPN.	USPAT	OR	ON	2007/08/03 19:02
S7	2	("5563290").URPN.	USPAT	OR	ON	2007/08/03 19:06
S8	3117	binap	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2007/08/03 19:18
S9	182	binap.clm.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2007/08/03 19:18
S10	2	sul??onated adj binap	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2007/08/03 19:33
S11	7	S9 and S2	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2007/08/03 19:33
S12	2	("5563290").URPN.	USPAT	OR	ON	2007/08/06 08:59
S13	1	("5274146").PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2007/08/06 09:30

## EAST Search History

S14	12	("5274146").URPN.	USPAT	OR	ON	2007/08/06 09:43
S15	1	("5274146").PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2007/08/06 11:03
S16	2	JP-2005255544-\$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2007/08/06 11:06
S17	2	((("5274146") or ("5324861"))).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2007/08/06 11:07
S18	7	("5324861").URPN.	USPAT	OR	ON	2007/08/06 11:08

We 8/6/07



chain nodes :

45 46 47 48 49 50 51 52 53 54

ring nodes :

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28  
29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44

chain bonds :

1-10 6-47 11-48 13-47 19-47 28-48 34-48 37-45 44-46 45-52 45-53 45-54 46-49 46-50 46-51

ring bonds :

1-2 1-6 2-3 2-40 3-4 3-37 4-5 5-6 7-8 7-12 8-9 8-44 9-10 9-42 10-11 11-12 13-14 13-18  
14-15 15-16 16-17 17-18 19-20 19-24 20-21 21-22 22-23 23-24 25-26 25-30 26-27 27-28  
28-29 29-30 31-32 31-36 32-33 33-34 34-35 35-36 37-38 38-39 39-40 41-42 41-43 43-44

exact/norm bonds :

37-45 44-46 45-52 45-53 45-54 46-49 46-50 46-51

exact bonds :

1-10 6-47 11-48 13-47 19-47 28-48 34-48

normalized bonds :

1-2 1-6 2-3 2-40 3-4 3-37 4-5 5-6 7-8 7-12 8-9 8-44 9-10 9-42 10-11 11-12 13-14 13-18  
14-15 15-16 16-17 17-18 19-20 19-24 20-21 21-22 22-23 23-24 25-26 25-30 26-27 27-28  
28-29 29-30 31-32 31-36 32-33 33-34 34-35 35-36 37-38 38-39 39-40 41-42 41-43 43-44

Match level :

1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom 11:Atom 12:Atom  
13:Atom

14:Atom 15:Atom 16:Atom 17:Atom 18:Atom 19:Atom 20:Atom 21:Atom 22:Atom 23:Atom  
24:Atom 25:Atom 26:Atom 27:Atom 28:Atom 29:Atom 30:Atom 31:Atom 32:Atom 33:Atom 34:Atom  
35:Atom 36:Atom 37:Atom 38:Atom 39:Atom 40:Atom 41:Atom 42:Atom 43:Atom 44:Atom 45:CLASS  
46:CLAS47:Atom 48:Atom 49:CLAS50:CLASS51:CLASS52:CLASS53:CLASS54:CLASS

hve  
8/6/2007

=> d his

(FILE 'HOME' ENTERED AT 11:00:05 ON 06 AUG 2007)

FILE 'REGISTRY' ENTERED AT 11:00:44 ON 06 AUG 2007

L1 STRUCTURE UPLOADED

L2 0 S L1

L3 4 S L1 SSS FULL

FILE 'HCAPLUS' ENTERED AT 11:02:15 ON 06 AUG 2007

L4 2 S L3

FILE 'STNGUIDE' ENTERED AT 11:03:26 ON 06 AUG 2007

FILE 'HCAPLUS' ENTERED AT 11:10:42 ON 06 AUG 2007

E US2006-211882/APPS

L5 0 S US2006-211882/APPS

L6 1 S US2006-211882/AP, PRN, PN

E L6 RN

FILE 'REGISTRY' ENTERED AT 11:12:14 ON 06 AUG 2007

L7 10 S 150273-68-0/RN OR 775352-14-2/RN OR 7732-18-5/RN OR 80-59-1/R

FILE 'HCAPLUS' ENTERED AT 11:15:00 ON 06 AUG 2007

L8 2 S 150273-68-0/RN OR 775352-14-2/RN

L9 3 S AMANO,A?/AU AND IGARASHI,D?/AU AND SAYO,N?/AU

*Mr. Smith*  
*8/6/07*

=&gt;

Uploading C:\Program Files\Stnexp\Queries\2007 cases\10550564\core str.str

L1 STRUCTURE UPLOADED

=&gt; d l1

L1 HAS NO ANSWERS

L1 STR

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

Structure attributes must be viewed using STN Express query preparation.

=&gt; s l1

SAMPLE SEARCH INITIATED 11:01:21 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 2 TO ITERATE

100.0% PROCESSED 2 ITERATIONS

0 ANSWERS

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*COMPLETE\*\*

BATCH \*\*COMPLETE\*\*

PROJECTED ITERATIONS: 2 TO 124

PROJECTED ANSWERS: 0 TO 0

L2 0 SEA SSS SAM L1 *←*

=&gt; s l1 sss full

FULL SEARCH INITIATED 11:01:36 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 71 TO ITERATE

100.0% PROCESSED 71 ITERATIONS

4 ANSWERS

SEARCH TIME: 00.00.01

L3 4 SEA SSS FUL L1 *←*

=&gt; d l3 1-4 ide

L3 ANSWER 1 OF 4 REGISTRY COPYRIGHT 2007 ACS on STN

RN 865062-26-6 REGISTRY

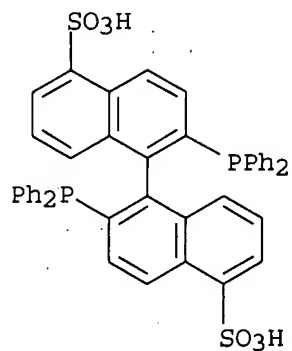
ED Entered STN: 11 Oct 2005

CN [1,1'-Binaphthalene]-5,5'-disulfonic acid, 2,2'-bis(diphenylphosphino)-  
(9CI) (CA INDEX NAME)

MF C44 H32 O6 P2 S2

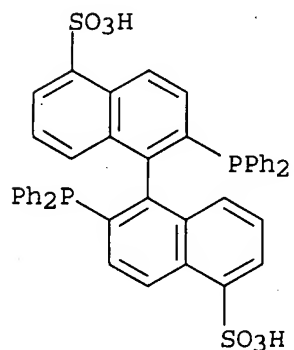
CI COM

SR CA



\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

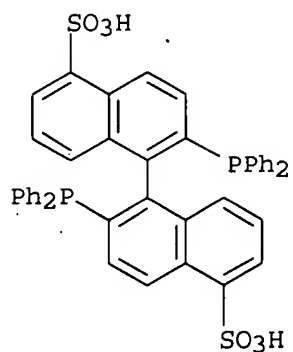
L3 ANSWER 2 OF 4 REGISTRY COPYRIGHT 2007 ACS on STN  
 RN 864956-92-3 REGISTRY  
 ED Entered STN: 11 Oct 2005  
 CN [1,1'-Binaphthalene]-5,5'-disulfonic acid, 2,2'-bis(diphenylphosphino)-,  
 disodium salt (9CI) (CA INDEX NAME)  
 MF C44 H32 O6 P2 S2 . 2 Na  
 SR CA  
 LC STN Files: CA, CAPLUS  
 CRN (865062-26-6)



● 2 Na

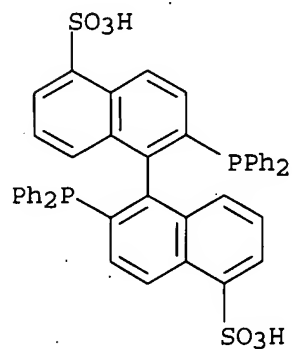
1 REFERENCES IN FILE CA (1907 TO DATE)  
 1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L3 ANSWER 3 OF 4 REGISTRY COPYRIGHT 2007 ACS on STN  
 RN 39341-59-4 REGISTRY  
 ED Entered STN: 05 Sep 2004  
 CN [1,1'-Binaphthalene]-5,5'-disulfonic acid, 2,2'-bis(diphenylphosphino)-,  
 (R)- (9CI) (CA INDEX NAME)  
 MF C44 H32 O6 P2 S2  
 CI COM  
 SR CA



\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

L3 ANSWER 4 OF 4 REGISTRY COPYRIGHT 2007 ACS on STN  
 RN 150271-78-6 REGISTRY  
 ED Entered STN: 23 Sep 1993  
 CN [1,1'-Binaphthalene]-5,5'-disulfonic acid, 2,2'-bis(diphenylphosphino)-, disodium salt, (R)- (9CI) (CA INDEX NAME)  
 MF C44 H32 O6 P2 S2 . 2 Na  
 SR CA  
 LC STN Files: CA, CAPLUS, USPATFULL  
 CRN (739341-59-4)



● 2 Na

1 REFERENCES IN FILE CA (1907 TO DATE)  
 1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> fil hcaplus  
 COST IN U.S. DOLLARS  
 FULL ESTIMATED COST

SINCE FILE	TOTAL
ENTRY	SESSION
180.80	181.01



10/550564 METHOD FOR PRODUCING OPTICALLY ACTIVE CARBOXYLIC

FILE 'HCAPLUS' ENTERED AT 11:02:15 ON 06 AUG 2007  
 USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.  
 PLEASE SEE "HELP USAGETERMS" FOR DETAILS.  
 COPYRIGHT (C) 2007 AMERICAN CHEMICAL SOCIETY (ACS)

*Reg# Search  
 huc 8/6/07*

Copyright of the articles to which records in this database refer is held by the publishers listed in the PUBLISHER (PB) field (available for records published or updated in Chemical Abstracts after December 26, 1996), unless otherwise indicated in the original publications. The CA Lexicon is the copyrighted intellectual property of the the American Chemical Society and is provided to assist you in searching databases on STN. Any dissemination, distribution, copying, or storing of this information, without the prior written consent of CAS, is strictly prohibited.

FILE COVERS 1907 - 6 Aug 2007 VOL 147 ISS 7  
 FILE LAST UPDATED: 5 Aug 2007 (20070805/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s 13

L4 2 L3 *X*

=> d 14 1-2 ibib abs

L4 ANSWER 1 OF 2 HCAPLUS COPYRIGHT 2007 ACS on STN  
 ACCESSION NUMBER: 2005:1020733 HCAPLUS  
 DOCUMENT NUMBER: 143:306189  
 TITLE: Preparation of pyridinecarboxamides with recyclable catalysts and without the use of halogenation agents  
 INVENTOR(S): Shimazu, Hidetaka; Tamashima, Tomoyuki  
 PATENT ASSIGNEE(S): Koei Chemical Co., Ltd., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 18 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2005255544	A	20050922	JP 2004-65682	20040309
PRIORITY APPLN. INFO.:			JP 2004-65682	20040309

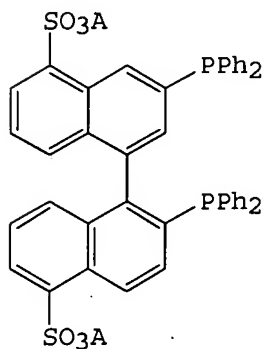
AB Pyridinecarboxamides are prepared by isomerization of pyridinealldoximes in multiphase solvent mixts. in the presence of (A) mixts. of hydrophilic phosphines and transition metals, or (B) water-soluble complexes comprising the phosphines and metals. Thus, 4-pyridinealldoxime was refluxed with sulfonated BINAP and RuCl<sub>2</sub>(cod) in 1-butyl-4-methylimidazolium PF<sub>6</sub> salt and C<sub>6</sub>H<sub>6</sub> for 24 h, then the ionic liquid was recovered, which was used in the same reaction 4 more times. Total yield of 4-pyridinecarboxamide was 94.5%.

L4 ANSWER 2 OF 2 HCAPLUS COPYRIGHT 2007 ACS on STN  
 ACCESSION NUMBER: 1993:581016 HCAPLUS

## 10/550564 METHOD FOR PRODUCING OPTICALLY ACTIVE CARBOXYLIC

DOCUMENT NUMBER: 119:181016  
 TITLE: Preparation of water-soluble alkali metal sulfonate-substituted binaphthylphosphine transition metal complexes and enantioselective hydrogenation method using them  
 INVENTOR(S): Ishizaki, Takerou; Kumobayashi, Hidenori  
 PATENT ASSIGNEE(S): Takasago International Corp., Japan  
 SOURCE: Eur. Pat. Appl., 9 pp.  
 CODEN: EPXXDW  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 544455	A1	19930602	EP 1992-310561	19921119
EP 544455	B1	19970212		
R: CH, DE, FR, GB, IT, LI				
JP 05170780	A	19930709	JP 1991-331535	19911121
JP 2736947	B2	19980408		
US 5274146	A	19931228	US 1992-977638	19921117
US 5324861	A	19940628	US 1993-116583	19930907
PRIORITY APPLN. INFO.:			JP 1991-331535	A 19911121
			US 1992-977638	A3 19921117
OTHER SOURCE(S):		CASREACT 119:181016; MARPAT 119:181016		
GI				



AB [M(X)<sub>n</sub>(Q)(SO<sub>3</sub>A-BINAP)]Y (M = Ru, Ir, Rh, Pd, etc.; SO<sub>3</sub>A-BINAP = tertiary phosphine represented by formula I (A = alkali metal atom), X = Cl, Br, iodo; n = 0, 1; Q = benzene or p-cymene, Y = Cl, Br, iodo, ClO<sub>4</sub>, PF<sub>6</sub>, BF<sub>4</sub>) were prepared and shown to be catalysts for the enantioselective hydrogenation of olefins, ketones, and imines.

=&gt; fil stng

COST IN U.S. DOLLARS

FULL ESTIMATED COST

SINCE FILE

ENTRY

10.86

TOTAL

SESSION

191.87

10/550564 METHOD FOR PRODUCING OPTICALLY ACTIVE CARBOXYLIC

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE  
ENTRY

TOTAL  
SESSION

CA SUBSCRIBER PRICE

-1.56

-1.56

FILE 'STNGUIDE' ENTERED AT 11:03:26 ON 06 AUG 2007  
USE IS SUBJECT TO THE TERMS OF YOUR CUSTOMER AGREEMENT  
COPYRIGHT (C) 2007 AMERICAN CHEMICAL SOCIETY (ACS)

FILE CONTAINS CURRENT INFORMATION.

LAST RELOADED: Aug 3, 2007 (20070803/UP).

<http://www.cas.org/support/stngen/stndoc/properties.html>

=> s 150273-68-0/RN or 775352-14-2/RN or 7732-18-5/RN or 80-59-1/RN or 1333-74-0/RN or 5309-52-4/RN or 16957-70-3/RN or 32231-50-8/RN or 49642-47-9/RN or 56006-48-5/rn

1 150273-68-0/RN  
1 775352-14-2/RN  
1 7732-18-5/RN  
1 80-59-1/RN  
1 1333-74-0/RN  
1 5309-52-4/RN  
1 16957-70-3/RN  
1 32231-50-8/RN  
1 49642-47-9/RN  
1 56006-48-5/RN

L7 10 150273-68-0/RN OR 775352-14-2/RN OR 7732-18-5/RN OR 80-59-1/RN  
OR 1333-74-0/RN OR 5309-52-4/RN OR 16957-70-3/RN OR 32231-50-8/R  
N OR 49642-47-9/RN OR 56006-48-5/RN

=> d 17 ide 1-10

L7 ANSWER 1 OF 10 REGISTRY COPYRIGHT 2007 ACS on STN

RN 775352-14-2 REGISTRY

ED Entered STN: 05 Nov 2004

CN Ruthenate(1-), [(1R)-2,2'-bis(diphenylphosphino-κP)[1,1'-binaphthalene]-5,5'-disulfonato(2-)]chloro[(1,2,3,4,5,6-η)-1-methyl-4-(1-methylethyl)benzene]-, sodium chloride (1:2:1) (9CI) (CA INDEX NAME)

MF C54 H44 Cl O6 P2 Ru S2 . Cl . 2 Na

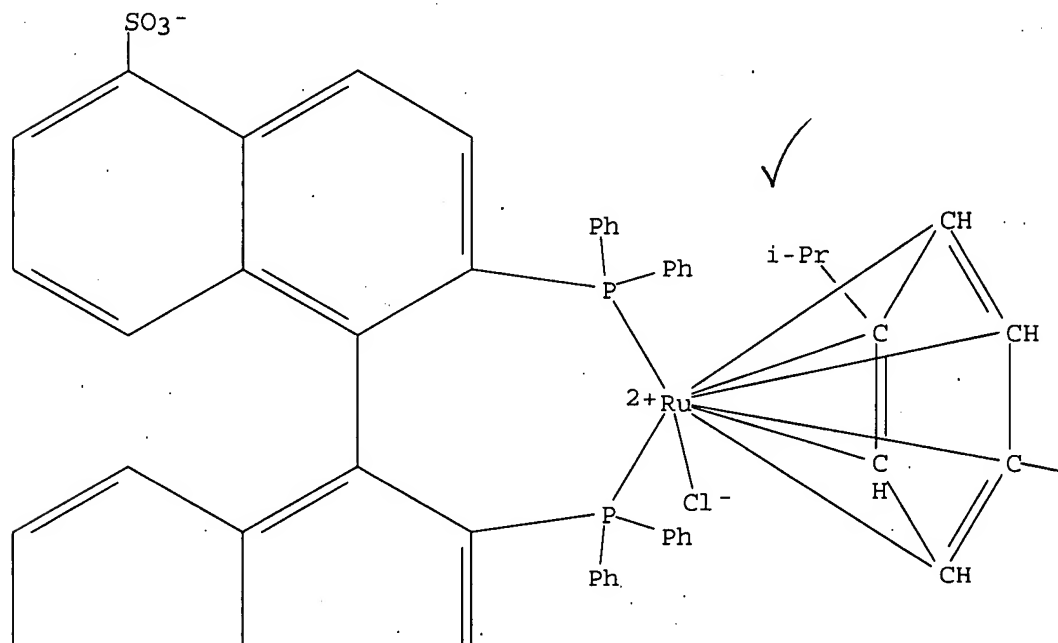
CI CCS

SR CA

LC STN Files: CA, CAPLUS, CASREACT, USPATFULL

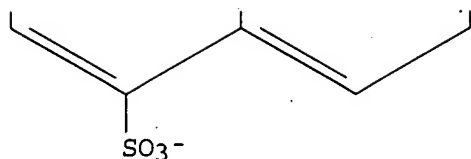
CRN (795269-49-7)

PAGE 1-A



PAGE 1-B

— Me



PAGE 2-A

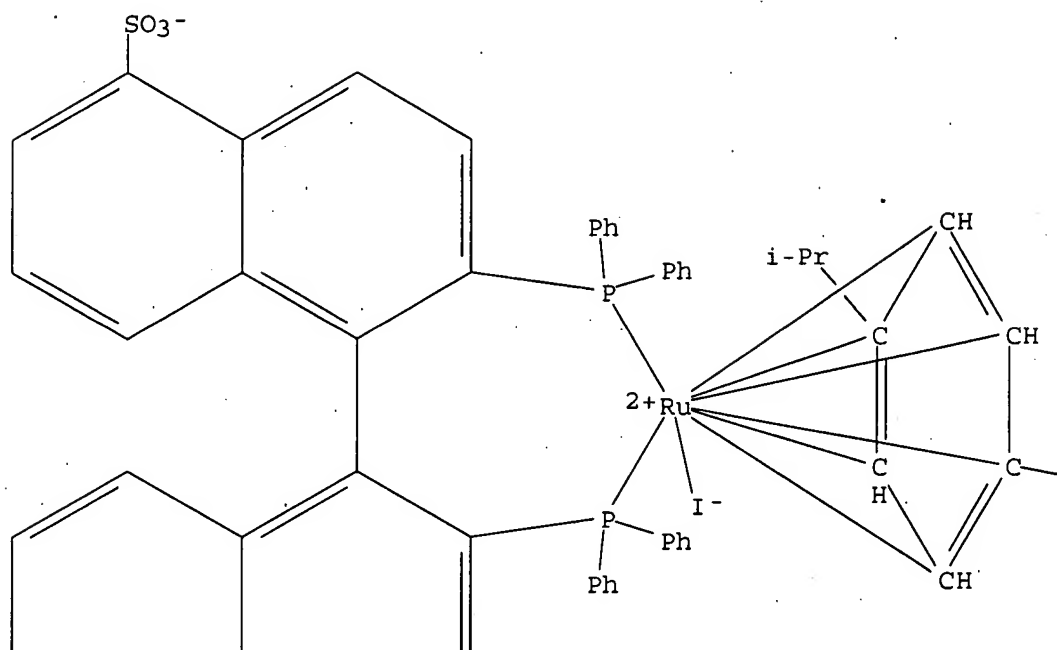
● Cl<sup>-</sup>

● 2 Na<sup>+</sup>

1 REFERENCES IN FILE CA (1907 TO DATE)  
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

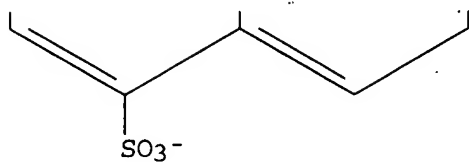
L7 ANSWER 2 OF 10 REGISTRY COPYRIGHT 2007 ACS on STN  
RN 150273-68-0 REGISTRY  
ED Entered STN: 23 Sep 1993  
CN Ruthenate(1-), [2,2'-bis(diphenylphosphino)[1,1'-binaphthalene]-5,5'-disulfonato(2-)-P,P']iodo[(1,2,3,4,5,6-η)-1-methyl-4-(1-methylethyl)benzene]-, sodium iodide (1:2:1), (R)- (9CI) (CA INDEX NAME)  
MF C54 H44 I O6 P2 Ru S2 . I . 2 Na  
CI CCS  
SR CA  
LC STN Files: CA, CAPLUS, CASREACT, USPATFULL  
CRN (762212-66-8)

PAGE 1-A



PAGE 1-B

Me



●  $\text{I}^-$

● 2  $\text{Na}^+$

2 REFERENCES IN FILE CA (1907 TO DATE)  
2 REFERENCES IN FILE CAPLUS (1907 TO DATE)

## 10/550564 METHOD FOR PRODUCING OPTICALLY ACTIVE CARBOXYLIC

=&gt; s 150273-68-0/RN or 775352-14-2/RN

2 150273-68-0

0 150273-68-0D

2 150273-68-0/RN

(150273-68-0 (NOTL) 150273-68-0D )

1 775352-14-2

0 775352-14-2D

1 775352-14-2/RN

(775352-14-2 (NOTL) 775352-14-2D )

L8

2 150273-68-0/RN OR 775352-14-2/RN

=&gt; d 18 ibib abs

L8 ANSWER 1 OF 2 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2004:857540 HCAPLUS

DOCUMENT NUMBER: 141:349812

TITLE: Stereoselective catalytic hydrogenation process for producing optically active carboxylic acids from  $\alpha,\beta$ -unsaturated carboxylic acids

INVENTOR(S): Amano, Akira; Igarashi, Daisuke; Sayo, Noboru

PATENT ASSIGNEE(S): Takasago International Corporation, Japan

SOURCE: PCT Int. Appl., 29 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004087632	A1	20041014	WO 2004-JP4373	20040326
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
GB 2414987	A	20051214	GB 2005-19756	20040326
GB 2414987	B	20061025		
CN 1753857	A	20060329	CN 2004-80004883	20040326
JP 2006521371	T	20060921	JP 2006-507695	20040326
US 2006211882	A1	20060921	US 2005-550564	20050926
IN 2005CN02777	A	20070608	IN 2005-CN2777	20051027
PRIORITY APPLN. INFO.:			JP 2003-89605	A 20030328
			WO 2004-JP4373	W 20040326

OTHER SOURCE(S): CASREACT 141:349812; MARPAT 141:349812

AB A hydrogenation method is described for producing an optically active carboxylic acid [e.g., (2R)-methylbutanoic acid] with a high optical purity is obtained by the hydrogenation of the corresponding  $\alpha,\beta$ -unsatd. carboxylic acid (e.g., tiglic acid) using a chiral ruthenium sulfonated BINAP hydrogenation catalyst [e.g., [RuI[p-cymene][(R)-(SO<sub>3</sub>Na)<sub>2</sub>BINAP]]I] complex; the complex catalyst used



10/550564 METHOD FOR PRODUCING OPTICALLY ACTIVE CARBOXYLIC

can be recovered and reused as an aqueous solution

REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

10/550564 METHOD FOR PRODUCING OPTICALLY ACTIVE CARBOXYLIC

*Inventor Search*  
*Aug 8/6/07*

FILE 'REGISTRY' ENTERED AT 11:12:14 ON 06 AUG 2007  
L7 10 S 150273-68-0/RN OR 775352-14-2/RN OR 7732-18-5/RN OR 80-59-1/R

FILE 'HCAPLUS' ENTERED AT 11:15:00 ON 06 AUG 2007  
L8 2 S 150273-68-0/RN OR 775352-14-2/RN

=> s amano,a?/au and igarashi,d?/au and sayo,n?/au  
416 AMANO,A?/AU  
30 IGARASHI,D?/AU  
107 SAYO,N?/AU  
L9 3 AMANO,A?/AU AND IGARASHI,D?/AU AND SAYO,N?/AU

=> d 19 1-3 ibib abs

L9 ANSWER 1 OF 3 HCAPLUS COPYRIGHT 2007 ACS on STN  
ACCESSION NUMBER: 2005:1130650 HCAPLUS  
DOCUMENT NUMBER: 143:405612  
TITLE: Preparation of chiral phosphines, transition metal complexes containing the same as the ligand, and process for production of optically active carboxylic acids  
INVENTOR(S): Amano, Akira; Igarashi, Daisuke; Sayo, Noboru  
PATENT ASSIGNEE(S): Takasago International Corporation, Japan  
SOURCE: PCT Int. Appl., 27 pp.  
CODEN: PIXXD2  
DOCUMENT TYPE: Patent  
LANGUAGE: Japanese  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005097811	A1	20051020	WO 2005-JP3117	20050225
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
US 2007060772	A1	20070315	US 2006-540166	20060929
PRIORITY APPLN. INFO.:			JP 2004-97508	A 20040330
			WO 2005-JP3117	A1 20050225
OTHER SOURCE(S):		MARPAT 143:405612		
GI				

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB Sulfonated phosphines represented by the general formula (I) (wherein X1 =

O, CH<sub>2</sub>; X<sub>2</sub> = CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, 1,2-dimethylethylene, isopropylidene, difluoromethylene; A = a Group IA alkali metal of the periodic table, hydrogen, an ammonium ion; a, b, c, d = 0 or 1, with the proviso that the cases wherein the sum of a, b, c, and d is 0 are excepted) are prepared. Desired optically active carboxylic acids of formula R<sub>1</sub>R<sub>2</sub>C\*HC\*HR<sub>3</sub>CO<sub>2</sub>H [\* denotes an asym. carbon atom; R<sub>1</sub>-R<sub>3</sub> = H, optionally branched cycloalkyl, each (un)substituted aromatic hydrocarbyl or heterocyclyl, acyloxy, acylamino, alkoxy, aryloxy, alkoxy-carbonyl, CO<sub>2</sub>H, furyloxy, thienyloxy; or R<sub>1</sub> and R<sub>2</sub> or R<sub>1</sub> and R<sub>3</sub> = (CH<sub>2</sub>)<sub>m</sub>-X<sub>3</sub>-(CH<sub>2</sub>)<sub>n</sub> (X<sub>3</sub> = CH<sub>2</sub>, N, O, S); m = 1,2; n = an integer of 0-3] are prepared from a carboxylic acid having a carbon-carbon double bond of formula R<sub>1</sub>R<sub>2</sub>C:CR<sub>3</sub>CO<sub>2</sub>H (R<sub>1</sub>-R<sub>3</sub> = same as above) through asym. hydrogenation with a catalyst consisting of a transition metal complex containing a water-soluble ligand I. The water soluble ligand I permits easy separation of the used catalyst from the product by liquid-liquid separation alone and enables the recovery of an expensive transition metal and the reuse of the catalyst. Thus, 2.52 g (R)-5,6,7,8,5',6',7',8'-octahydro-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl [(R)-H<sub>8</sub>-BINAP] was added to 3.68 g concentrated H<sub>2</sub>SO<sub>4</sub> at 0-5°, stirred, followed by adding 35.8 g 30% SO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> via a syringe, and the mixture was warmed to room temperature, stirred for 1 h, stored at 5° for 2 wk, added slowly to crushed ice (200 g), neutralized by adding dropwise 50% NaOH at ≤15°, distilled to completely remove water under reduced pressure to give a solid (62 g). The solid was stirred with 140 mL 10% aqueous MeOH solution for 1 h, filtered to remove sodium sulfate, and concentrated to give 3.2 g (R)-SO<sub>3</sub>Na-H<sub>8</sub>-BINAP (II) [a+b+c+d = 2 (32%), a+b+c+d = 3 (53%)]. II (0.13 g), 38.3 mg [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub>, and 3 mL MeOH were mixed and stirred at room temperature for 24 h, followed evaporation of the solvent to give 0.19 g 0.17 mg [RuCl((R)-SO<sub>3</sub>Na-H<sub>8</sub>-BINAP)(p-cymene)]Cl (III). Tiglinic acid (3.3 g), 2.42 mg III, 4 mL diisopropyl ether, and 3 mL distilled water were heated at 80° and H pressure of 2.5 MPa for 2 h in an autoclave to give 2.9 g (R)-2-methylbutanoic acid (96.4% ee).

REFERENCE COUNT: 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 2 OF 3 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2005:1075754 HCAPLUS

DOCUMENT NUMBER: 143:378576

TITLE: Preparation of optically active transition metal/diamine complex and process for producing optically active alcohol with the complex

INVENTOR(S): Amano, Akira; Igarashi, Daisuke; Sayo, Noboru

PATENT ASSIGNEE(S): Takasago International Corporation, Japan

SOURCE: PCT Int. Appl., 64 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

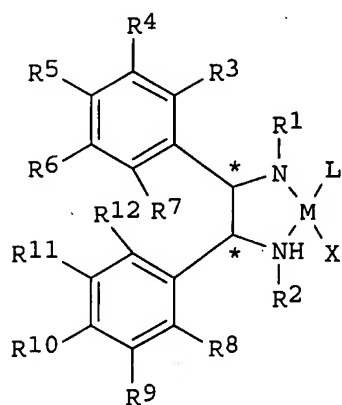
FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

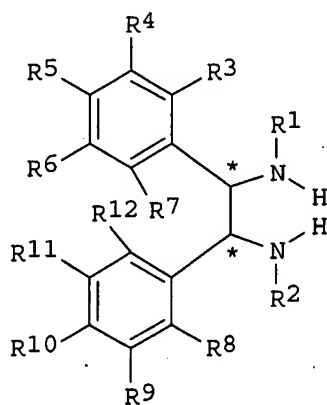
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005092830	A1	20051006	WO 2005-JP5728	20050328
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,				

GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW  
 RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

US 2007149831 A1 20070628 US 2006-594744 20060929  
 PRIORITY APPLN. INFO.: JP 2004-96472 A 20040329  
 WO 2005-JP5728 W 20050328  
 OTHER SOURCE(S): MARPAT 143:378576  
 GI



I



II

AB A water-soluble, optically active transition metal/diamine complex represented by the general formula (I) [wherein R1 and R2 each represents hydrogen, a hydrocarbon group, -SO2R13 (wherein R13 = optionally substituted hydrocarbon group, substituted amino, camphoryl); R3 to R12 each represents hydrogen, an each optionally substituted hydrocarbon group, alkoxy, aryloxy, or aralkyloxy or substituted amino; M represents a transition metal; X represents halogeno; L represents a ligand; and \* indicates asym. carbon; provided that at least one of R3 to R7 and R8 to R12 is substituted amino] and an optically active diamine compound (II) (R2-R13) constituting the ligand of the complex are prepared. The optically active transition metal/diamine complex is useful as a catalyst for asym. synthesis and can be easily separated from reaction products through liquid separation, etc. and is recyclable. A process for producing an optically active alc. comprises using the catalyst I for asym. reduction of a ketone. Thus, a solution of 26.76 g 4-dimethylaminobenzaldehyde in 80 mL THF was added to a mixture of 10.4 g hydrazine sulfate, 78 mL H2O, and 28% aqueous NH3 at ≤40° over 2 h, stirred at ≤40° for 2-3 h, treated with 28% aqueous NH3 to make the aqueous layer alkali, treated with 100 mL toluene, cooled to 10°, and filtered to give 19.75 g 4,4'-bis(dimethylamino)benzazine (III) (83.9%). A mixture of Zn powder (19.6 g) and 300 mL THF was treated dropwise with 28.45 g TiCl4 III at -40° over 40 min at ≤40°, stirred at the same temperature for 30 min and then at -30 to -25° for 1 h, treated with 8.82 g III at -25°, stirred for 3 h while the temperature was raised to room temperature,

and left to stand overnight to give, after workup, crude 1,2-bis[4-(dimethylamino)phenyl]ethane-1,2-diamine (IV). IV (3.48 g) was converted into the HCl salt and then back into racemic free amine (1.04 g) which was separated twice by HPLC using a Chiralcel OD-H column to give 63.1 mg (1R,2R)-1,2-bis[4-(dimethylamino)phenyl]ethane-1,2-diamine which (50 mg) was mixed with 17.7 mg Et<sub>3</sub>N in 1 mL CH<sub>2</sub>Cl<sub>2</sub>, treated with portionwise with a solution of 28.1 mg benzenesulfonyl chloride in 1 mL CH<sub>2</sub>Cl<sub>2</sub> under ice-cooling, and stirred at the same temperature for 1 h to give, after purification

by TLC, 57.4 mg (1R,2R)-N-(benzenesulfonyl)-1,2-bis[4-(dimethylamino)phenyl]ethane-1,2-diamine (V). A mixture of V (4 mg), 1.86 mg [RuCl<sub>2</sub>(mesitylene)]<sub>2</sub>, 0.45 g sodium formate, and 4 mL H<sub>2</sub>O was treated with 0.2 g acetophenone, stirred at 50° for 2.5 h to give 0.19 g (R)-1-phenethyl alc. (optical purity 90.78% ee).

REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 3 OF 3 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2004:857540 HCAPLUS

DOCUMENT NUMBER: 141:349812

TITLE: Stereoselective catalytic hydrogenation process for producing optically active carboxylic acids from  $\alpha,\beta$ -unsaturated carboxylic acids

INVENTOR(S): Amano, Akira; Igarashi, Daisuke; Sayo, Noboru

PATENT ASSIGNEE(S): Takasago International Corporation, Japan

SOURCE: PCT Int. Appl., 29 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004087632	A1	20041014	WO 2004-JP4373	20040326
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
GB 2414987	A	20051214	GB 2005-19756	20040326
GB 2414987	B	20061025		
CN 1753857	A	20060329	CN 2004-80004883	20040326
JP 2006521371	T	20060921	JP 2006-507695	20040326
US 2006211882	A1	20060921	US 2005-550564	20050926
IN 2005CN02777	A	20070608	IN 2005-CN2777	20051027
PRIORITY APPLN. INFO.:			JP 2003-89605	A 20030328
			WO 2004-JP4373	W 20040326

OTHER SOURCE(S): CASREACT 141:349812; MARPAT 141:349812

AB A hydrogenation method is described for producing an optically active carboxylic acid [e.g., (2R)-methylbutanoic acid] with a high optical

purity is obtained by the hydrogenation of the corresponding  $\alpha,\beta$ -unsatd. carboxylic acid (e.g., tiglic acid) using a chiral ruthenium sulfonated BINAP hydrogenation catalyst [e.g.,  $[\text{RuI}[\text{p-cymene}][(\text{R})-(\text{SO}_3\text{Na})_2\text{BINAP}]]\text{I}$ ] complex; the complex catalyst used can be recovered and reused as an aqueous solution

REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT